G-19512

SECOND ANNUAL TECHNICAL REPORT

AND

FINAL REPORT

NSF GRANT G-19512

to

Georgia Institute of Technology
Atlanta, Georgia 30332

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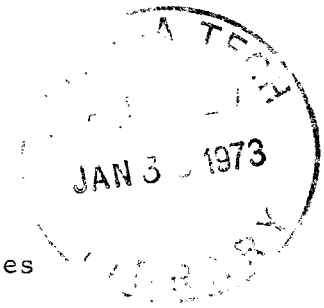
Magnetic Rotation Spectra of Simple Molecules



August 15, 1964

Preface

Our original proposal of February 9, 1961 laid out a five-year program of studies on the subject of Magnetic Rotation Spectra of Simple Molecules. The generous support provided by NSF Grant G-19512, for a two-year period, has permitted us to follow that proposal closely.

Our First Annual Technical Report of November 7, 1962, outlined progress made under this grant to that time and also indicated the directions we intended pursuing. Our research proposal submitted on March 11, 1963, requesting continuation of this grant, expanded on these intentions. Our efforts since that time have followed these lines closely.

General Summary

Our apparatus has been completely rebuilt around a Jarrell-Ash 3.4 Meter Ebert Spectograph and an electromagnet providing a working space of 6" diameter and 70 cm length with a magnetic field intensity up to 2400 oersted. This system has been used with both straight-through, single-pass optics and with a multiple reflection cell which gives a 3.5 meter path inside the field.

Systems previously found to exhibt a magnetic rotation spectrum have been examined at higher resolution with this apparatus, specifically, ICl, IBr, glyoxal, $CSCl_2$, SO_2, and CS_2. Other systems have been examined, with limited success. Although excellent data has been obtained on these systems, the analysis of this data has proceeded very

slowly in part because of the complexity of the problem and in part because the resolution provided by this instrument is still less than really needed.

Specific Comments

The spectrum of ICl has been carefully re-examined, excellent plates are available, but we have been unable to analyze the spectrum in the particularly interesting region near the dissociation limit. Resolution is adequate for this problem, and it is hoped that further efforts can be devoted to this analysis in the future.

The spectrum of IBr has been re-examined at high resolution and an analysis of this spectrum is nearly complete. The problem is particularly complicated because the rotational branches observed contain only a small number of lines and several different vibrational bands are superposed and badly jumbled. It is hoped that this analysis will be completed by the end of the present summer, 1964, and the results published.

The spectrum of glyoxal has been restudied and again considerable effort devoted to its analysis but without convincing success. In this case we are seriously hindered by limited resolution.

The spectrum of thiophosgene, $CSCl_2$, has been studied in some detail, and a partial vibrational analysis has been obtained. Our results have been used by Dr. J. C. D. Brand and his associates in Glasgow (shortly at Vanderbilt University) in separating the singlet from the triplet spectrum. There is a great deal more information in the spectrum than has been incorporated in the vibrational analysis of either Brand's group or ourselves, and we have not yet published our results in the hope of elucidating these details.

A magnetic rotation spectrum was found for the 3800A bands in SO_2 by Dr. Brinkley Snowden in our laboratory. A partial analysis of this system was reported at the Symposium on Molecular Spectroscopy in June, 1964. Further efforts are in progress to obtain a convincing analysis of both this system and the system around 2900A. Unfortunately, here we are operating at the limits of resolution of our apparatus, and really need an additional order of magnitude resolution. Thus, refinements of our suggested analysis require estimates of several parameters, specifically the molecular geometry and spin-coupling parameters, and a computer synthesis of the expected spectrum. This process is extremely time-consuming.

The spectrum of CS_2 has been examined at high resolution, but no analysis has been achieved.

In addition to these studies on stable species, a program has been instituted on the spectrum of radicals generated by high-frequency discharge and flash photolysis. It is hoped that this technique will permit not only study of radicals, but will also make possible studies of stable species at much higher fields obtained by pulses in

a simple solenoid.

Paralleling this experimental program, theoretical aspects of the phenomenon itself and the magnetic properties of triplet states have been studied.

Mr. Jerry Whitten devised a clever approximation to atomic orbitals in terms of Gaussian functions and used this approximation to calculate the spin-spin and spin-rotation coupling parameters in glyoxal in the hope that an a priori calculation of these quantities would permit an analysis of the spectrum. These calculations constitute the basis of his doctoral dissertation.

Dr. Vedeen Smith worked in our laboratory for a period of six months in a rather unsuccessful attempt to extend the theory of magnetic rotation spectra, but during this period contributed extensively to our understanding of the existent theory.

Future Program

As indicated above, many of the studies we have undertaken are incomplete. We anticipate continuing these studies with the broad objectives indicated in our Proposal of March 11, 1963:

1) to elucidate the fundamental nature of the phenomenon by continued study of high-resolution spectra of gases in the electronic region of the spectrum,

2) to attempt to understand the details of excited triplet states of simple molecules by study of the high-resolution spectra of such systems as we now have accessible, and

3) to search for further applications of the technique in the area of gas-phase, electronic spectra.

The NSF grant GP-2408, based on our Proposal of March, 1963, should permit us to continue and hopefully, conclude, many of the studies described here. We appreciate the confidence of the National Science Foundation in continuing this support.

Personnel

The program has involved the following individuals:

1. Mr. Wayne Sullivan, who studied the spectra of ICl and IBr during the summers of 1962, 63, and 64. Mr. Sullivan graduated from the Georgia Institute of Technology with a B.S. degree in Chemistry in June, 1964. Next year he will study at the Eidgenoschene Technische Hochschule in Zurich, Switzerland.

2. Mr. William Miller, who studied the spectrum of $CSCl_2$ in part during the summer of 1963 following his graduation with a B.S. degree in Chemistry. Mr. Miller is now studying for the Ph.D. at Harvard University.

3. Mr. Arnold Stalder, who devoted part-time during the year and summer of 1962 as an undergraduate to preliminary studies of spectra of molecular fragments generated by radio-frequency discharge. He is now on a NASA Fellowship and is working towards his Ph.D. in this area.

4. Dr. Jerry Whitten, who was supported during the last year of his doctoral program. He is now on a post-doctoral research appointment at Princeton University.

5. Dr. Vedeen Smith, Ph.D. Physics, Georgia Institute of Technology, 1962, who contributed to our theoretical understanding of the phenomenon during the period February through August, 1963. He is now in Sweden with Professor Lowdoin.

6. Dr. Brinkley S. Snowden, Ph.D., Vanderbilt, 1963, who is responsible for the work on SO_2 and CS_2. He will continue with us until June, 1965.

Communications

a. Publications

Jerry L. Whitten, Journal of Chemical Physics, 39, 349 (1963)
"Gaussian Expansion of Wavefunctions"

Although this paper does not appear to be directly related to the program, it provides the basis for more immediately related calculations of Dr. Whitten's dissertation.

b. Theses

Jerry L. Whitten, August, 1963

"Theoretical Studies of Electronic States of Simple Polyatomic Molecules."

Part I. Gaussian Expansion of Wavefunctions.
Part II. Magnetic Interactions in the Triplet State of Glyoxal.

c. Talks and Seminars by W. H. Eberhardt

1. Invited paper at the Southeastern-Southwestern Regional Meeting of the American Chemical Society, New Orleans, December, 1961.

2. Vanderbilt University Chemistry Seminar, November, 1962.

3. Johns Hopkins University Chemistry Seminar, February, 1963.
4. duPont Research Laboratories, February, 1963.
5. Emory University NSF Summer Institute, special lecture, August, 1963.
6. Harvard University, three lectures, November, 1963.
7. Minnesota Section American Chemical Society, February, 1964.
8. Yale University Chemistry Seminar, February, 1964.
9. Columbia University Chemistry Seminar, April, 1964.
10. Division of Pure Physics, National Research Council of Canada, Ottawa, Seminar, April, 1964.

d. Papers Presented

"Magnetic Rotation Spectrum of SO_2", Brinkley S. Snowden and W. H. Eberhardt, Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, Ohio, June, 1964.